2a–c: Prepared by esterification of benzyl 4-hydroxybutyrate[3] with appropriate *N*-Boc-protected amino acids (*N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC), 4-dimethylaminopyridine (DMAP), CH_2Cl_2) followed by hydrogenolysis of the benzyl ester (H_2, 10% Pd on C, EtOH).

Modified benzhydrylamine resin: Benzhydrylamine resin (0.9 mol -NH_2 per gram) was coupled with Fmoc-6-aminohexanoic acid (TPTU, *i*$PrNEt_2$, DMF; Fmoc = 9-fluorenylmethoxycarbonyl), and the Fmoc protecting group was subsequently cleaved (20% piperidine in DMF). Excess reagents were used in all solid-phase reactions (1.2–1.5 $mmol\,g^{-1}$). After the reactions were complete, the resins were repeatedly washed with DMF, *i*PrOH, and Et_2O. Solutions of product obtained after detachment of the resins were filtered through a minimal amount of neutral alumina (activity grade 3) and evaporated to dryness under reduced pressure.

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Structural Diversity in the Solid-State Structures of the Rubidium and Cesium Salts of 2,6-Dimesitylphenylphosphane[**]

Gerd W. Rabe,[*] Sohrab Kheradmandan,
Louise M. Liable-Sands, Ilia A. Guzei, and
Arnold L. Rheingold

*Dedicated to Professor Wolfgang A. Herrmann
on the occasion of his 50th birthday*

We recently focused our interest on the heavier alkali metal derivatives of primary and secondary phosphanes with the general formula MPR_2 and MPRH, respectively. In light of numerous reports on lithium derivatives[1] and a few examples of sodium[2] and potassium[2c, 3] derivatives of MPR_2 and MPRH species, the dearth of structural data available on derivatives of rubidium and cesium is surprising. Recently, the solid-state structure of a sterically congested cesium silyl(fluorosilyl)phosphanide aggregate was reported.[2d] Heavier alkali metal phosphides are important because of their enhanced reactivity over their lithium counterparts, and also with respect to the structural diversity of their solid-state structures. We presented earlier a preliminary[3] and a full report[4] on the molecular structures of $[MP(H)Mes^*]_x$ species ($M = K–Cs$; $Mes^*PH_2 = 2,4,6\text{-}t\text{Bu}_3C_6H_2PH_2$, "supermesitylphosphane"[5]) as well as several different base adducts of these compounds. We also reported crystal structure determinations of three different base adducts of an asymmetrically substituted potassium phosphide, KP(*t*Bu)Ph.[6] All of these alkali metal derivatives exhibit infinitely extended, one-dimensional polymeric M–P ladder-type arrangements in the solid state.

Motivated by our recent findings, we have now extended our studies to heavier alkali metal derivatives of other sterically demanding primary phosphanes. We decided to employ the 2,6-dimesitylphenyl (Dmp) substituent,[7] since earlier work has suggested that this ligand is even more bulky than the Mes* ligand.[8] However, recent studies have indicated that the steric relationship between Dmp and Mes* is not as simple as once thought.[9] The preparation of the corresponding phosphane, $DmpPH_2$, was described recently.[10]

Reaction of equimolar amounts of rubidium or cesium metal with $DmpPH_2$ in THF at room temperature produced the yellow-orange RbP(H)Dmp and yellow CsP(H)Dmp complexes, respectively. Even in the presence of excess alkali

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[*] Dr. G. W. Rabe, Dipl.-Chem. S. Kheradmandan
Anorganisch-chemisches Institut
der Technischen Universität München Lichtenbergstrasse 4,
D-85747 Garching (Germany)
Fax: (+49) 89-289-13125
E-mail: g.rabe@lrz.tu-muenchen.de

L. M. Liable-Sands, Dr. I. A. Guzei, Prof. A. L. Rheingold
Department of Chemistry, University of Delaware
Newark, DE 19716 (USA)

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metal, bismetalation was not observed. Both RbP(H)Dmp and CsP(H)Dmp were fully characterized by ^{1}H and ^{31}P NMR, IR, and UV/Vis spectroscopy, and elemental analysis. Crystals suitable for an X-ray crystal structure determination were obtained by slow evaporation of a solution of RbP(H)Dmp in toluene. Crystals of CsP(H)Dmp were obtained from toluene/THF/*N*-methylimidazole (*N*-MeIm). The composition of both species was determined crystallographically as $[\{RbP(H)Dmp\}_4 \cdot C_7H_8]$ (**1**) (Figure 1) and $[\{Cs^+Cs_2[P(H)Dmp]_3^- \cdot 1/3\,C_7H_8\}_x]$ (**2**) (Figures 2 and 3).

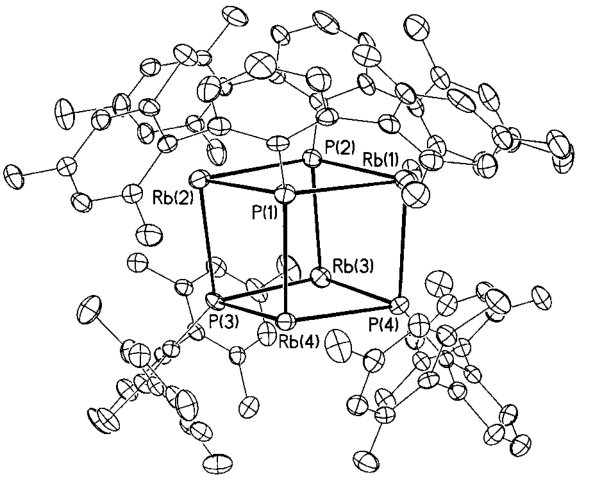

Figure 1. ORTEP diagram of the structure of **1** in the crystal. The hydrogen atoms and the toluene molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rb(1)–P(1) 3.756(2), Rb(1)–P(2) 3.411(2), Rb(1)–P(4) 3.399(2), Rb(2)–P(1) 3.520(2), Rb(2)–P(2) 3.473(2), Rb(2)–P(3) 3.558(2), Rb(3)–P(2) 3.579(2), Rb(3)–P(3) 3.425(2), Rb(3)–P(4) 3.516(2), Rb(4)–P(1) 3.454(2), Rb(4)–P(3) 3.412(2), Rb(4)–P(4) 3.480(2); P(1)-Rb(1)-P(2) 84.32(5), P(1)-Rb(1)-P(4) 96.00(5), P(2)-Rb(1)-P(4) 83.62(5), P(1)-Rb(2)-P(2) 87.10(5), P(1)-Rb(2)-P(3) 101.66(5), P(2)-Rb(2)-P(3) 79.31(5), P(2)-Rb(3)-P(3) 79.67(5), P(2)-Rb(3)-P(4) 79.57(5), P(3)-Rb(3)-P(4) 87.86(5), P(1)-Rb(4)-P(3) 106.11(5), P(1)-Rb(4)-P(4) 100.28(5), P(3)-Rb(4)-P(4) 88.64(5).

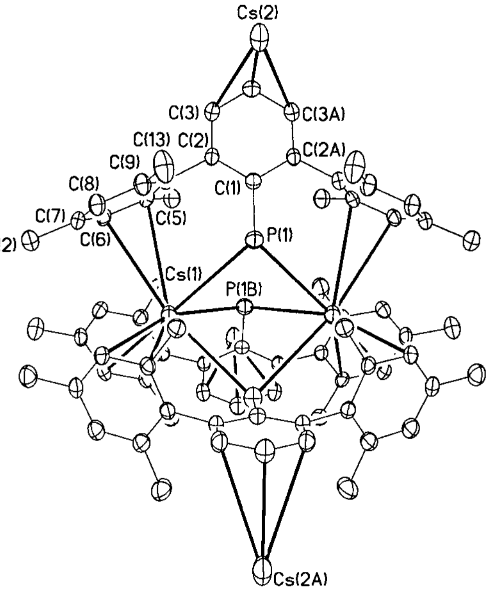

Figure 2. ORTEP diagram of the asymmetric unit of **2**. The hydrogen atoms and the toluene molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cs(1)–P(1) 3.6254(14), Cs(1)–Cs(1A) 4.8959(9); P(1)-Cs(1)-P(1A) 79.40(3), Cs(1)-P(1)-Cs(1A) 84.94(4), C(1)-P(1)-Cs(1) 117.33(13).

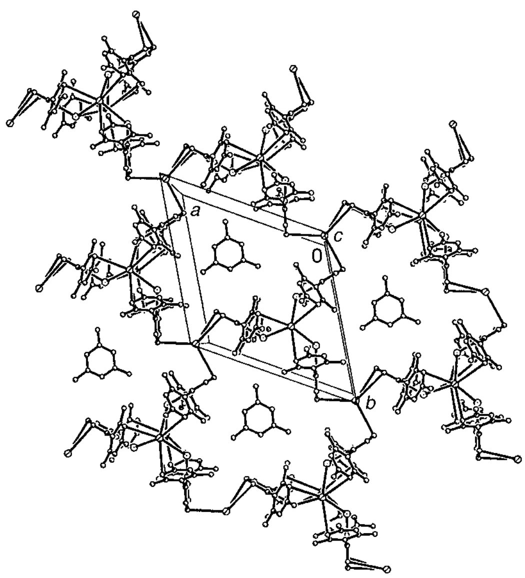

Figure 3. Unit-cell packing diagram of **2** showing the two-dimensional extension of the polymeric framework.

RbP(H)Dmp is slightly soluble in toluene at room temperature, which enabled crystallization from this solvent. It is noteworthy that CsP(H)Dmp is insoluble in toluene and can only be dissolved in the presence of classical Lewis bases such as THF, pyridine, or *N*-MeIm.

The molecular structure of **1** in the crystalline state (Figure 1) features a cubic arrangement of rubidium and phosphorus atoms with both mesityl rings of all four Dmp ligands "solvating" neighboring rubidium atoms with different degrees of π-interaction. Each rubidium cation in the Rb_4P_4 cube is therefore surrounded by three phosphide ligands and, additionally, "solvated" through π-bonding of two adjacent mesityl rings (from different Dmp ligands). The shortest Rb–C(ring) distances are Rb(1)–C(20) 3.216(7), Rb(2)–C(120) 3.401(7), Rb(3)–C(209) 3.425(7), and Rb(4)–C(318) 3.299(7) Å. The Rb–P interatomic separations range from 3.399(2) Å to 3.756(2) Å and can be compared to the corresponding distances found in polymeric $[RbP(H)Mes^*]_x$ (3.381(1)–3.504(1) Å).[4] The deviation from ideal cubic geometry is most readily seen by inspecting the interatomic angles within the Rb_4P_4 cube. The P-Rb-P angles range from 79.31(5)° to 106.11(5)°, the corresponding Rb-P-Rb angles from 75.91(4)° to 101.17(5)°, and the Rb–Rb distances from 4.2896(10) Å to 5.3954(12) Å. It is noteworthy that both the ^{1}H and the ^{31}P NMR spectra of **1** appear to be more or the less solvent-independent, indicating that the heterocubane framework of **1** may be retained in solution.

The solid-state structure of **2** (Figures 2 and 3) differs significantly from the cubic arrangement in **1**, exhibiting a novel and rather peculiar structural motif that also differs significantly from polymeric arrangements in other MP(H)R and MPR_2 species. In contrast to the infinitely extended parallel M–P ladder-type polymers of $[MP(H)Mes^*]_x$ (M = K–Cs) or the cubic arrangement in **1**, the extended structure of **2** consists of a polymeric two-dimensional framework of $Cs^+\{Cs_2[P(H)Dmp]_3\}^-$ contact ion pairs. Contrary to the coordination behavior of polymeric $[CsP(H)Mes^*]_x$, there are no *N*-MeIm ligands coordinated to the cesium cations in the solid-state structure of **2**.

The molecular structure of **2** in the crystalline state was solved in the hexagonal space group $P6_3/m$. The polymeric two-dimensional network of **2** shows two types of cesium cations, Cs(1) and Cs(2). Cs(1) and Cs(1A) lie on a threefold axis and are bridged by three phosphide ligands (Figure 2) with a Cs–P interatomic separation of 3.6254(14) Å, a P-Cs-P angle of 79.40(3)°, and a Cs-P-Cs angle of 84.94(4)°. Atom P(1) lies on a mirror plane. The interatomic Cs–P separation in **2** compares well with the corresponding distances found in polymeric $[CsP(H)Mes^*]_x$[4] (3.577(1)–3.642(1) Å), and the Cs–P interatomic separations in the recently reported cesium silyl(fluorosilyl)phosphanide (3.517(6) and 3.536(7) Å).[2d] In addition to three Cs(1)–P bonds, each Cs(1) cation is encapsulated by two ring carbon atoms (C(5) and C(6)) of three neighboring mesityl ligands with Cs(1)–C distances of 3.569(4) Å and 3.532(4) Å, respectively. These distances can be compared to the corresponding Cs–C interatomic separations in $[CsP(H)Mes^*]_x$ that range from 3.219(5) to 3.710(5) Å.[4]

Atom Cs(2) lies on a $\bar{6}$ axis and appears to be a bare cesium cation, "solvated" only by π-coordination of three arene ligands, each of them coordinated to the metal center in an η^3-fashion with Cs(2)–C distances of 3.655(5) Å (C(3) and C(3A)) and 3.332(8) Å (C(4)). The interaction of the large cesium cation Cs(2) with three separate $\{Cs_2[P(H)Dmp]_3\}^-$ ions gives a coordination environment reminiscent of a paddle-wheel. It is unique, has no precedence in organocesium chemistry, and differs considerably from the coordination environment around cesium observed in the molecular structures of the bent cesiocene triple-decker anion $[Cp_3Cs_2]^-$,[11] as well as the π-solvates $CsC(SiMe_3)_3 \cdot 3.5\,C_6H_6$[12a] and $CsSi(SiMe_3)_3 \cdot 1.5\,PhMe$.[12b] π-Interaction of aromatic systems with the heavier alkali metal cations has wide precedence in the literature,[2d, 6, 12] and was also observed in the molecular structures of the potassium, rubidium, and cesium derivatives $[MP(H)Mes^*]_x$.[3, 4] It should be noted that the Cs(2)–C distances in **2** are significantly shorter than the corresponding distances in the previously reported π-solvates $CsC(SiMe_3)_3 \cdot 3.5\,C_6H_6$ (av 3.81(2) Å)[12a] and $CsSi(SiMe_3)_3 \cdot 1.5\,PhMe$ (av 3.80(2) Å).[12b]

Crystals of **2** contain one toluene molecule per asymmetric unit with the methyl carbon atom equally disordered over three positions. The packing diagram of **2** (Figure 3) shows how every Cs(2) atom bridges three anionic $Cs_2[P(H)Dmp]_3$ moieties, thereby forming what appears to be a host–guest solid-state arrangement. Each molecule of toluene lies on a $\bar{6}$ axis in the center of a cavity formed by three $Cs^+\{Cs_2[P(H)Dmp]_3\}^-$ units.

This work demonstrates that the structural motifs found in the phosphides of the heavier alkali metals vary widely, determined both by the steric bulk of the phosphide ligand as well as the alkali metal cation employed.

Experimental Section

The compounds described below were handled under nitrogen using Schlenk line double-manifold, high-vacuum, glovebox (M.Braun, Labmaster 130) techniques. All solvents were dried before use.

RbP(H)Dmp (**1**): In the glovebox, a solution of $DmpPH_2$[10] (200 mg, 0.58 mmol) in THF (10 mL) was added to one equivalent of rubidium (50 mg, 0.58 mmol) in THF (5 mL), which resulted in a slow color change to orange. The reaction mixture was stirred for 4 h, centrifuged, the solvent removed, and the residues washed with hexane. The product crystallized from hot toluene and was dried under vacuum to afford **1** as a yellow-orange powder (150 mg, 60%). Compound **1** is well-soluble in THF and pyridine, slightly soluble in toluene at room temperature, and insoluble in aliphatic hydrocarbons. ^{1}H NMR (400 MHz, [D$_6$]benzene, 25°C, TMS): $\delta = 1.75$ (d, ^1J(P,H) = 180 Hz, 1H), 2.24 (s, 6H), 2.25 (s, 12H), 6.80 (d, ^3J (H,H) = 7 Hz, 2H), 6.85 (s, 4H), 6.95 (t, ^3J (H,H) = 7 Hz, 1H); ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C, TMS): $\delta = 1.67$ (d, ^1J(P,H) = 176 Hz, 1H), 2.13 (s, 12H), 2.26 (s, 6H), 6.27 (d, ^3J (H,H) = 7 Hz, 2H), 6.34 (t, ^3J (H,H) = 7 Hz, 1H), 6.78 (s, 4H); ^{31}P NMR (161.9 MHz, [D$_6$]benzene, 25°C): $\delta = -115.7$ (d, ^1J(P,H) = 180 Hz); ^{31}P NMR (161.9 MHz, [D$_8$]THF, 25°C): $\delta = -117.0$ (d, ^1J(P,H) = 176 Hz); elemental analysis: $C_{24}H_{26}PRb$: calcd: C 66.90, H 6.08; found: C 66.30, H 5.90; IR (Nujol): $\tilde{\nu} = 2250$ (s), 1882 (w), 1704 (w), 1569 (s), 1277 (w), 1243 (m), 1040 (s), 1014 (m), 999 (w), 853 (vs), 786 (w), 720 (m), 592 (w) cm^{-1}; UV/Vis (THF): λ_{max} (ε) = 212 (25000) nm.

CsP(H)Dmp (**2**): Compound **2** was prepared in a similar way to **1** with equimolar amounts of $DmpPH_2$[10] (200 mg, 0.58 mmol) and cesium (77 mg, 0.58 mmol). A slow color change to orange was observed. Workup of the reaction mixture gave **2** after crystallization from THF/hexane (1/1) at −30°C as a yellow powder (166 mg, 60%). Compound **2** is well-soluble in THF and pyridine, but insoluble in toluene and aliphatic hydrocarbons. ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C, TMS): $\delta = 1.79$ (d, ^1J(P,H) = 173 Hz, 1H), 2.12 (s, 12H), 2.26 (s, 6H), 6.26 (d, ^3J (H,H) = 7 Hz, 2H), 6.33 (t, ^3J (H,H) = 7 Hz, 1H), 6.78 (s, 4H); ^{31}P NMR (161.9 MHz, [D$_8$]THF, 25°C): $\delta = -99.9$ (d, ^1J(P,H) = 173 Hz); ^{133}Cs NMR (52.46 MHz, [D$_8$]THF, 25°C): $\delta = 34.8$; elemental analysis: $C_{24}H_{26}CsP$: calcd: C 60.26, H 5.48; found: C 60.04, H 5.25; IR (Nujol): $\tilde{\nu} = 2260$ (s), 1605 (w), 1571 (s), 1243 (m), 1176 (w), 1110 (w), 1087 (m), 1040 (s), 1010 (m) 990 (m), 850 (s), 784 (m), 730 (s), 720 (s), 593 (m) cm^{-1}; UV/Vis (THF): λ_{max} (ε) = 213 (26500), 247 (sh, 6100) nm.

Crystal structure data for **1**: $C_{103}H_{112}P_4Rb_4$, $M_r = 1811.66$, triclinic, space group $P\bar{1}$, $a = 14.2999(2)$, $b = 15.9550(2)$, $c = 23.3811(1)$ Å, $\alpha = 93.2838(1)$, $\beta = 103.6992(2)$, $\gamma = 107.0832(2)$°, $V = 4907.66(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.226$ g cm^{-3}, $F(000) = 1868$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 228(2)$ K, $\mu(Mo_{K\alpha}) = 2.090$ mm^{-1}, $R_1 = 0.0720$, $wR_2 = 0.2280$ for 14890 independent observed reflections ($I > 2\sigma(I)$, $1.8° \leq 2\Theta \leq 48.0°$), GOF = 1.043.

Crystal structure data for **2**: $C_{79}H_{86}Cs_3P_3$, $M_r = 1527.12$, hexagonal, space group $P6_3/m$, $a = 14.65280(10)$, $b = 14.65280(10)$, $c = 19.9405(3)$ Å, $V = 3707.73(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.368$ g cm^{-3}, $F(000) = 1540$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 218(2)$ K, $\mu(Mo_{K\alpha}) = 1.571$ mm^{-1}, $R_1 = 0.0540$, $wR_2 = 0.1414$ for 2940 independent observed reflections ($I > 2\sigma(I)$, $3.2° \leq 2\Theta \leq 56.5°$), GOF = 1.257.

The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2. Semiempirical ellipsoid absorption corrections were applied to the data sets. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atom on the phosphorus atoms in **1** and **2** could not be located from the difference map and were ignored. All other hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHELXTL (5.3) program library (G. M. Sheldrick, Siemens XRD, Madison, WI). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100686. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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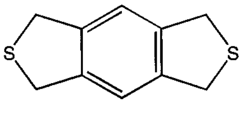
Self-Assembly of Lamellar and Expanded Lamellar Coordination Networks**

George K. H. Shimizu,* Gary D. Enright,
Chris I. Ratcliffe, John A. Ripmeester, and
Danial D. M. Wayner

The construction of infinite solid-state arrays by employing coordinate covalent bonding and the principles of self-assembly has resulted in numerous metal–ligand networks with fascinating structural topologies.[1] Among the framework types that have resulted are PtS analogues,[1a] honeycomb structures,[1b] α-Po analogues,[1c] diamondoid networks,[1f, j] and $SrSi_2$ analogues.[1g] With these metallo-organic networks, one hopes to realize the wealth of applications known for solely inorganic frameworks, which range from separations[2] to catalysis[3] to devices.[4] The preponderance of infinite arrays formed by metal coordination chemistry employ either aromatic N-donor ligands[1a, d, i, j, 5] or cyano-derived ligands[1b, e, 6] as the metal-chelating point of contact. Thioethers have been largely neglected as ligands in this sense,[7] probably due to the relatively poor metal-complexing ability of nonchelating thioethers.[8] Herein, we introduce a family of layered coordination networks, structurally reminiscent of anionic clays,[9] generated by the self-assembly of a novel dithia ligand with $AgBF_4$. Single-crystal data on two lamellar arrays are presented which illustrate the formation and expansion of the layers. Differential scanning calorimetry (DSC) results reveal thermal stability to over 180 °C, which is attributed to a "lamellar chelate effect."



1

The dithia ligand **1** contains two sulfurs linked by a rigid durene unit, which prohibits chelation of both donors to a single metal center. The ligand **1** was synthesized in excellent yield by the reaction of tetrabromodurene with sodium sulfide. An equimolar mixture of **1** and $AgBF_4$ was stirred for three hours in MeCN, and then benzene was diffused into this solution to afford colorless platelike crystals of $[\{Ag(\mathbf{1})(MeCN)_2\}_\infty][BF_4]_\infty$ (**2**), suitable for X-ray diffraction analysis. An infinite two-dimensional layered structure is formed by the cationic $\{Ag(\mathbf{1})(MeCN)_2\}$ building blocks while the BF_4 anions reside between the parallel layers (Figure 1).

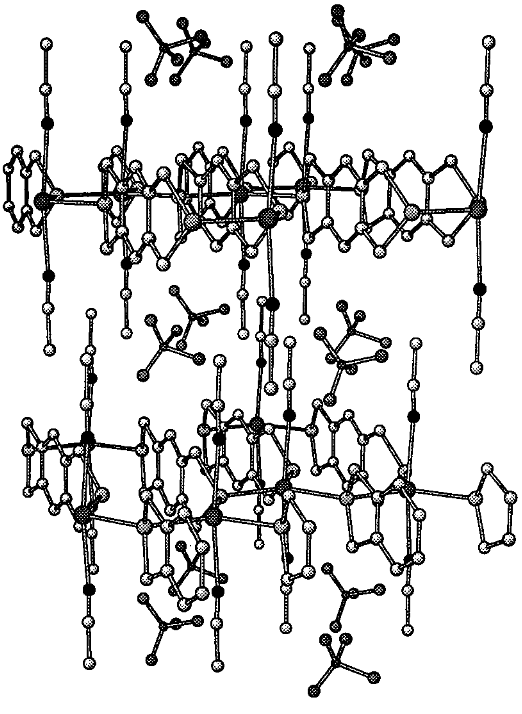


Figure 1. Structure of **2** in the crystal, showing the lamellar network with interlayer BF_4 ions and MeCN molecules that point into the interlayer region. Hydrogen atoms are omitted for clarity.

The coordination geometry about the Ag^I ions is a trigonal bipyramid comprising three equatorial sulfur donors and two axially bound MeCN molecules. Remarkably, in order to achieve such a structure, it is necessary for the highly symmetrical **1** to be asymmetrically coordinated to three Ag^I ions. Figure 2 clearly shows that one thioether group of **1** coordinates a single Ag^I center, while the sulfur atom on the

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[*] Dr. G. K. H. Shimizu, Dr. G. D. Enright, Dr. C. I. Ratcliffe,
Dr. J. A. Ripmeester, Dr. D. D. M. Wayner
Steacie Institute for Molecular Sciences
National Research Council of Canada
100 Sussex Drive, Ottawa, Ontario K1A 0R6 (Canada)
Fax: (+1) 613-991-4278
E-mail: shimizu@ned1.sims.nrc.ca

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